Molecular Complexes. Part XIV.[1] Crystal and Molecular Structure of the π^*-Electron-acceptor Molecule 1,2,4,5-Tetracyanobenzene

By **C. Keith Prout** * and **Ian J. Tickle**, Chemical Crystallography Laboratory, Oxford University, South Parks Road, Oxford OX1 3QS

Crystals of the title compound are monoclinic, unit-cell dimensions a = 6·51, b = 13·79, c = 10·44, γ = 112·0, spacegroup $P2_1/b$, Z = 4. The crystal and molecular structure has been determined from visually estimated three-dimensional photographic data by direct methods and refined by full-matrix least squares to R 0·091 for 880 independent reflections. After correction for rigid-body motion the mean C≡N, C–CN, and C–C(benzene ring) bond lengths are 1·140, 1·446, and 1·401 Å. The internal angles in the benzene ring are significantly different from 120°.

ALTHOUGH the crystal structures of a number of π–π^* electron-donor–acceptor complexes of 1,2,4,5-tetracyanobenzene[2] have been determined, the molecular dimensions of this electron acceptor are not accurately known because these complexes have either contained heavy atoms or have been disordered. We report the crystal and molecular structure of 1,2,4,5-tetracyanobenzene itself.

EXPERIMENTAL

1,2,4,5-Tetracyanobenzene was prepared by the method of ref. 3. The crystalline product had a blue tint, probably due to phthalocyanine dye type impurity, which could not be removed by recrystallising from methyl ethyl ketone, acetone, or ethanol or by treatment with activated charcoal. However, the crystals (quite substantial plates) gave excellent X-ray diffraction patterns. The elemental analysis was satisfactory (Found: C, 67·2; H, 1·15; N, 32·1. Calc. for $C_{10}H_2N_4$: C, 67·4; H, 1·13; N, 31·5%). Colourless crystals could be obtained by passing a solution of the crude product in acetone through an alumina column. This sample, presumably of higher purity gave, from various solvents, only very thin fragile plates unsuitable for X-ray work.

Unit-cell dimensions were obtained from calibrated zero-layer Weissenberg and precession photographs. The intensities of 880 independent reflections from layers 0—5kl were estimated visually from multiple-film equi-inclination Weissenberg photographs and placed on a common scale from the known exposure times with a stabilised X-ray source and standardised development conditions. Intensities were corrected for Lorentz and polarisation effects but not absorption or extinction.

Crystal Data. $C_{10}H_2N_4$, $M = 178·2$. Monoclinic, $a = 6·51 \pm 0·03$, $b = 13·79 \pm 0·05$, $c = 10·44 \pm 0·03$ Å, $\gamma = 112·0 \pm 0·3°$, $U = 869·3$ Å^3; $D_m = 1·35$ (by flotation) $Z = 4$, $D_c = 1·361$. Spacegroup $P2_1/b$ (C^5_{2h}, No. 14; 1st setting) Cu-K_α radiation, $\lambda = 1·5418$ Å; μ(Cu-K_α) = 7·4 cm^{-1}. Crystal size 0·6 × 0·4 × 0·1 mm.

Normalised structure amplitudes (E values) were computed (B 3·5 Å^3) and their distribution statistics found to be those of a hypercentric system. This is consistent with a structure in which the 1,2,4,5-tetracyanobenzene molecules of high point-symmetry lie at general positions in the unit cell. From 149 non-equivalent E values $>1·4$, 973 triple products ($>1·5$) were generated. The reflections 1,0,3 (E 3·89), 1,$\overline{10}$,8 (E 4·291), and 3,$\bar{1}$,9 (E 3·918) were arbitrarily assigned positive signs to define the origin, one reflection (2,0,6, E 2·131) was found to have positive sign (from Σ_1 interactions). The reflections 2,0,5 and 1,4,4 were assigned symbolic phases. Following the symbolic addition process of Karle and Karle[4] the signs of 101 reflections were determined with probabilities $>0·9975$. The acceptable probability was then lowered to 0·953

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[1] Part XIII, B. Mayoh and C. K. Prout, *J.C.S. Faraday II*, 1972, **68**, 1072.

[2] J. D. Wright and P. Murray-Rust, *J. Chem. Soc.* (*C*), 1968, 247; B. Kamenar, C. K. Prout, and J. D. Wright, *J. Chem. Soc.* (*A*), 1966, 661; S. Kumekura, F. Iwasuki, and Y. Saito, *Bull. Chem. Soc. Japan*, 1957, **40**, 1826; C. K. Prout, I. J. Tickle, and J. D. Wright, following paper.

[3] A. S. Bailey, B. R. Henn, and J. M. Langdon, *Tetrahedron*, 1963, **19**, 661.

[4] J. Karle and I. L. Karle, *Acta Cryst.*, 1966, **21**, 849.

and a further 27 signs were determined. At this stage it became clear that 2,0,5 had a negative sign and 1,4,4 positive. A Fourier synthesis computed from the set of 128 signed reflections showed an isometric array of peaks from which a complete molecule could be unambiguously located.

On the assumption of individual isotropic temperature factors the atomic co-ordinates from the E map were refined by full-matrix least squares, first three cycles with unit weights then three cycles with the weighting scheme $w = [1 + (F_o/5)^2]^{-1}$. At this stage (R 0·124) the two hydrogen atoms were located from a difference-Fourier map and a further five cycles of full-matrix least-squares refinement of all atomic parameters except those for the hydrogen atoms were completed assuming anisotropic thermal motion. The final R was 0·092 (for observed reflections). In the final difference-Fourier synthesis the σ of the electron density was 0·16 eÅ^{-3} and all spurious peaks had less than twice this electron density.

TABLE 1

Atomic co-ordinates ($\times 10^4$) and thermal parameters ($\times 10^3$) * with standard deviations in parentheses

	x/a	y/b	z/c	U_{11}	U_{22}	U_{33}	$2U_{23}$	$2U_{31}$	$2U_{12}$
C(1)	5801(7)	2903(4)	460(4)	49(3)	47(3)	42(3)	9(4)	−4(4)	27(4)
C(2)	6188(8)	3160(4)	528(4)	51(3)	49(3)	39(2)	10(4)	1(4)	47(4)
C(3)	8015(8)	3861(4)	1175(5)	53(3)	52(3)	55(3)	−13(5)	−2(4)	45(4)
C(4)	9461(7)	3461(4)	1739(4)	47(3)	47(3)	45(3)	−5(4)	0(4)	33(4)
C(5)	9088(7)	2392(4)	1667(4)	49(3)	53(3)	42(3)	2(4)	−1(4)	49(5)
C(6)	7238(8)	1690(4)	1021(5)	57(3)	49(3)	48(3)	7(4)	−3(4)	34(4)
C(7)	3918(8)	1392(4)	−237(5)	56(3)	51(3)	60(3)	8(5)	−10(4)	36(5)
C(8)	4623(10)	3544(4)	−66(5)	67(4)	60(3)	56(3)	0(5)	−3(5)	63(5)
C(9)	11,417(8)	4138(4)	2414(5)	58(3)	53(3)	64(3)	−26(5)	−19(5)	42(5)
C(10)	10,589(9)	1997(4)	2270(5)	63(4)	54(3)	56(3)	−10(5)	−9(5)	54(5)
N(1)	2448(8)	829(4)	−801(5)	73(3)	74(3)	79(4)	3(6)	−41(5)	25(5)
N(2)	3336(9)	3801(4)	−539(5)	74(4)	92(4)	76(3)	−3(6)	−24(5)	99(6)
N(3)	12,970(8)	4620(4)	2958(5)	67(3)	71(3)	95(4)	−41(6)	−35(5)	44(5)
N(4)	11,843(9)	1716(5)	2742(5)	85(4)	96(4)	72(3)	−25(6)	−38(5)	115(6)
				U_{iso}					
H(1)	696	90	95	60					
H(2)	845	464	123	60					

The temperature factor T is given by: $T = \exp[(-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{23}klb^*c^* + 2U_{13}hla^*c^* + 2U_{12}hka^*b^*)]$.

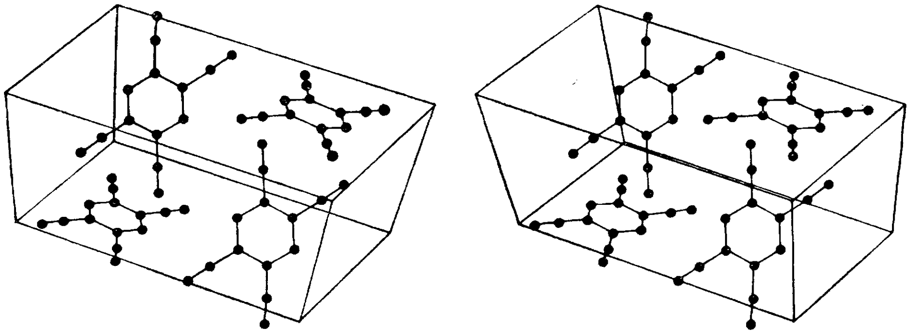

FIGURE 1 General stereoscopic projection. The transformation matrix from the orthogonal crystal axes, a, b^*, and c, to a set of orthogonal axes X, Y, and Z with Z perpendicular to the plane of the paper is:

$$\begin{array}{ccc} 0{\cdot}602 & 0{\cdot}583 & -0{\cdot}545 \\ 0{\cdot}696 & 0{\cdot}718 & 0{\cdot}000 \\ 0{\cdot}392 & 0{\cdot}380 & 0{\cdot}838 \end{array}$$

Supplementary publication SUP No. 20595 (7 pp., 1 microfiche) * lists the observed structure amplitudes and the structure factors calculated from the final atomic parameters in Table 1.

All calculations were performed on the Oxford University KDF 9 computer with either Rollett and Hodder's NOVTAPE [5] or Rollett and Ford's ALGOL [6] systems. Atomic scattering factors for neutral atoms were taken from ref. 7.

RESULTS AND DISCUSSION

The crystals are built up from isolated 1,2,4,5-tetracyanobenzene molecules in general positions in the unit cell which is shown in stereoscopic projection in Figure 1. The bond lengths, interbond angles, and the shorter non-bonded intermolecular contacts are listed in Tables 2—4.

The anisotropic temperature factors are consistent with the assumption that the molecule vibrates as a rigid body whose motion can be defined by two symmetrical tensors the one, T, describing the linear oscillating motion of the centre of libration of the molecule and the other, ω, describing the angular oscillating motion about this centre, which for a molecule in a

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* For details see Notice to Authors No. 7 in *J. Chem. Soc.* (*A*), 1970, Issue No. 20 (items less than 10 pp. are sent as full size copies).

[5] J. S. Rollett and O. J. R. Hodder, unpublished work.

[6] J. S. Rollett and G. Ford, unpublished work.

[7] 'International Tables for *X*-Ray Crystallography,' vol. 3, Kynoch Press, Birmingham, 1962.

TABLE 2

Bonded distances (Å), with and without correction for libration; standard deviations are in parentheses

	Uncorrected	Corrected
C(1)–C(2)	1·398	1·403(7)
C(1)–C(6)	1·385	1·391(7)
C(1)–C(7)	1·442	1·445(7)
C(2)–C(3)	1·394	1·400(8)
C(2)–C(8)	1·452	1·455(8)
C(3)–C(4)	1·388	1·393(8)
C(4)–C(5)	1·404	1·408(7)
C(4)–C(9)	1·449	1·452(8)
C(5)–C(6)	1·403	1·408(8)
C(5)–C(10)	1·430	1·433(8)
C(7)–N(1)	1·144	1·146(8)
C(8)–N(2)	1·138	1·139(8)
C(9)–N(3)	1·132	1·134(8)
C(10)–N(4)	1·139	1·140(8)
C(3)–H(2)	1·01	
C(6)–H(1)	1·05	

TABLE 3

Interbond angles (deg.) with standard deviations in parentheses

C(6)–C(1)–C(2)	121·2(5)	C(9)–C(4)–C(5)	117·9(5)
C(7)–C(1)–C(2)	120·3(5)	C(4)–C(5)–C(6)	121·1(5)
C(6)–C(1)–C(7)	118·5(5)	C(4)–C(5)–C(10)	120·1(5)
C(1)–C(2)–C(3)	121·7(5)	C(10)–C(5)–C(6)	118·8(5)
C(1)–C(2)–C(8)	119·2(5)	C(5)–C(6)–C(1)	117·5(5)
C(8)–C(2)–C(3)	119·1(5)	C(1)–C(7)–N(1)	178·8(6)
C(2)–C(3)–C(4)	117·3(5)	C(2)–C(8)–N(2)	177·0(7)
C(3)–C(4)–C(5)	121·2(5)	C(4)–C(9)–N(3)	176·2(6)
C(3)–C(4)–C(9)	120·4(5)	C(5)–C(10)–N(4)	177·6(6)

TABLE 4

Intermolecular contacts (Å) <3·4 Å

N(1) ··· C(3^{I})	3·21	N(3) ··· C(6^{IV})	3·33
N(1) ··· C(4^{I})	3·16	N(3) ··· C(7^{IV})	3·30
N(1) ··· C(9^{I})	3·14	N(3) ··· N(4^{V})	3·32
N(2) ··· C(4^{II})	3·37	N(4) ··· C(2^{VI})	3·16
N(2) ··· C(10^{I})	3·30	N(4) ··· C(8^{VI})	3·36
N(2) ··· N(2^{III})	3·39		

Atomic parameters obtained from those in Table 1 by the following translations:

I $1 - x, \frac{1}{2} - y, z - \frac{1}{2}$
II $x - 1, y, z$
III $1 - x, 1 - y, -z$
IV $x + 1, \frac{1}{2} + y, \frac{1}{2} - z$
V $x, \frac{1}{2} + y, \frac{1}{2} + z$
VI $2 - x, \frac{1}{2} - y, \frac{1}{2} + z$

TABLE 5

Analysis of rigid-body thermal motion

Principal axes	Vectors of T or matrix relative to:					
	Inertial axes			Orthogonal crystal axes †		
(a) T Tensor/Å^2						
0·049(2)	0·9403	0·3403	−0·0039	0·7081	0·4813	0·5167
0·044(2)	−0·3387	0·9370	0·0858	−0·5351	0·8432	−0·0520
0·036(3)	0·0329	−0·0794	0·9963	−0·4607	−0·2396	0·8546
	Inertial axes			Orthogonal crystal axes †		
(b) ω Tensor/deg.^{2}						
29(6)	0·9800	−0·0483	0·1932	0·7280	0·0764	0·6813
4·6(1·3)	0·1638	0·7470	−0·6443	0·2962	0·8612	−0·4131
9·2(1·0)	−0·1132	0·6631	0·7400	−0·6183	0·5025	0·6043

ω Tensor origin relative to centre of gravity −0·18(10), 0·00(5), −0·29(10) Å

† a, b^*, and c.

general position in the unit cell need not coincide with the centre of gravity.[8] The T and ω tensors are specified in Table 5. The most significant libration is about an axis roughly parallel to the inertial axis bisecting the C(1)–C(2) bond. Cruickshank's libration correction [9] has been applied to bond lengths.

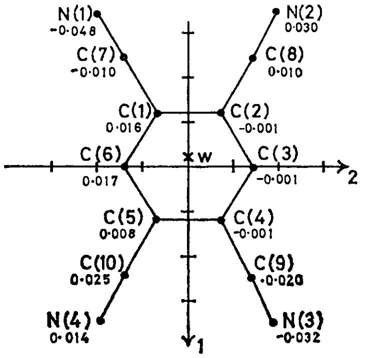

FIGURE 2 Projection on the molecular plane showing atom numbering, deviations from the least squares best plane, inertial axes, and origin of ω tensor

The molecule is generally planar but of the four cyano-groups two [C(8)–N(2) and C(10)–N(4)] are slightly above the plane (Figure 2) and two [C(7)–N(1) and C(9)–N(3)] slightly below, as if from a mutual repulsion. However, there is little supporting evidence from the angles of C(1), C(2), C(4), and C(5) to suggest overcrowding of the cyanide groups. Although in a general position the point-symmetry of the molecule is barely significantly different from *mmm* (D_{2h}), the molecule is more symmetric than those observed in molecular complexes [2] but the differences are explicable in terms of the larger experimental errors in these structures.

The mean C–N bond length (1·140 Å) is the same as that found in *cis*-1,2,3-tricyanocyclopropane,[10] within the spread of values found in tetracyanothiophen,[11] and not significantly different from the values observed in various dicyanomethylene derivatives.[12] The mean C–CN distance (1·446 Å) agrees very well with that found in *cis*-1,2,3-tricyanocyclopropane and other

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[8] G. S. Pawley, *Acta Cryst.*, 1963, **16**, 1204.

[9] D. W. J. Cruickshank, *Acta Cryst.*, 1956, **9**, 757.

[10] A. Hartman and F. L. Hirschfeld, *Acta Cryst.*, 1966, **20**, 80.

[11] V. Rychnovsky and D. Britton, *Acta Cryst.*, 1968, *B*,**24**, 725.

[12] See bibliography in, ' Molecular Structure and Dimensions,' vols. 1 and 3, ed. O. Kennard and D. G. Watson, N. V. Oosthoek's, Utrecht, 1971, 1972.

nitriles. The length is intermediate between the expected sp–sp^2 1·419 Å and sp–sp^3 1·459 Å carbon–carbon bond lengths.[13] The carbon–carbon bond lengths in the benzene nucleus (mean 1·401 Å) agree very well with the mean values (1·398 Å, after libration correction) found in benzene by neutron diffraction[14] at 138 K although they are in general a little (not significantly) longer than those found for benzene by X-ray work.[15]

The benzene ring shows considerable angular distortion. The internal angles at C(1), C(2), C(4), and C(5), *i.e.* those carbon atoms carrying the cyanide groups, are greater than 120° (mean 121·3°), all equivalent and significantly greater than those at C(3) and C(6) (mean 117·4°) which in turn are equivalent. The enlargement of the interval ring angle at an aromatic carbon atom carrying an electrophilic substituent, an effect commonly observed in nitrobenzenes, appears to be a rather general structural consequence of the presence of these substituents.

We thank the S.R.C. for a Studentship (to I. J. T.).

[2/1669 *Received, 14th July, 1972*]

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[13] B. P. Stoecheff, *Tetrahedron*, 1962, **17**, 135.

[14] G. E. Bacon, N. A. Curry, and S. A. Wilson, *Proc. Roy. Soc.*, 1964, *A*, **279**, 98.

[15] E. G. Cox, D. W. J. Cruickshank, and J. A. S. Smith, *Proc. Roy. Soc.*, 1958, *A*, **247**, 1.